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A core level spectroscopic study on RNi_2B_2C (R = Y, Er) borocarbides

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Abstract : Polycrystalline samples of YNi_2B_2C and magnetic $ErNi_2B_2C$ were prepared by arc-melting technique with a T_c ~15 K Core level spectroscopic studies have been performed in order to see the valence of Y, Er and Ni. The results show that Ni and Er exists in 2+ valence state and Y exists in 3+ valence state.

Keywords : Borocarbides, spectroscopic studies, superconductivity

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The quarternary borocarbide intermetallic compounds RNi_2B_2C where R is a rare-earth element exhibit a wide variety of physical properties. The structure of these compounds is body-centered tetragonal (space group 14/mmm) with alternating square planar layers of rare-earth carbides and corrugated Ni_2B_2 sheets with a unit cell consisting of two formula units [1], their physical properties depending upon the R atom. However, their electronic structure is not 2D but it is 3D like in case of the conventional superconductors [2,3]. They behave like type-II superconductors with a small coherence length (~50–100 Å). Electronic structure calculations on YNi_2B_2C show that the states near the Fermi Level (E_F) are dominated mainly by the Ni ($3d$) character and have a relatively high density of states at E_F and the superconductivity is believed to originate in the Ni_2B_2 layers [4]. The estimation of λ_{ph} and T_c within the rigid ion approximation indicates that the superconductivity in YNi_2B_2C can be well accounted for by the conventional phonon mechanism [4]. The presence of the $3d$ transition metal Ni and its layered crystal structure raise intriguing questions about the origin of superconductivity in them. Hence the study of Ni core-level

assumes great importance. As is well known, introduction of ferromagnetic elements cause depression of T_c, superconductors with ferromagnetic elements such as Fe, Co or Ni as one of the constituents have low T_c. In borocarbides also, T_c has been found to decrease by partial substitution of other transition metals for Ni in YNi_2B_2C [5–7] and in $ErNi_2B_2C$ [8]. Further, only a few nickel-containing binary superconductors are known in the literature and their T_c are less than 5 K. Also, Ni being a Jahn-Teller ion and known to exhibit mixed valency, makes this study all the more interesting.

Here, we report the results of our XPS study on the core levels of YNi_2B_2C and $ErNi_2B_2C$ polycrystalline samples.

Materials were prepared by standard arc-melting techniques. Detailed method of preparation and characterization results have been published elsewhere [9]. The core-level photoemission studies were carried out on an X-ray photoelectron spectrometer (VG Microtech MT 300). The spectra were taken with non-monochromatic but monoenergetic Al Kα x-radiation. Calibration of the spectrometer was done using the Ag ($3d_{5/2}$) peak at 367.9 eV. The total instrumental resolution in all the measurements was 0.80 eV. Fresh surfaces needed for measurements were obtained by mechanically scraping and sputtering the sample surface in UHV. No shift due to charging was observed in any of the core-level spectra recorded.

The resistivity of the samples were measured and their superconducting transition temperature was found to be 15.7 K for YNi_2B_2C and 10.5 K for $ErNi_2B_2C$, for the latter superconductivity coexists with magnetism below 6.5 K (T_N ~6.5 K).

The binding energies of the core levels for the two samples YNi_2B_2C and $ErNi_2B_2C$ are measured and analyzed. The spectra of B 1*s* and Ni 2*p* for both the samples, Y 3d for YNi_2B_2C and Er 4*d* for $ErNi_2B_2C$ are shown in the Figures (1–4) respectively.

C 1s core level :

After deconvolution of the C 1*s* core level spectra, we observed three peaks at energies ~285 eV, ~286 eV, ~287 eV in YNi_2B_2C and ~285 eV, ~286 eV, ~289 eV in $ErNi_2B_2C$. The peak at ~285 eV arises from compounds having predominantly C–C and C–H type bonds, the other peaks at ~286 eV and ~287 eV arise from compounds having C–O type bonds and the peak at ~289 eV arises from compounds having C=O type bonds.

These peaks are likely to be from the carbon impurity on the surface of the sample. It is very difficult to remove carbon impurities from the sample completely by scraping. However, this can be done by repeated sputtering by Argon ions but since carbon is there in the lattice itself, repeated sputtering changes the stoichiometry of the sample and consequently may also affect its properties. Therefore, we are not reporting the carbon spectra in our results.

B 1s core level :

The main B 1*s* core level peak is found to be at 192.7 eV and 192.4 eV for YNi_2B_2C and $ErNi_2B_2C$ respectively (Figure 1). The energy corresponding to pure Boron for B 1*s*

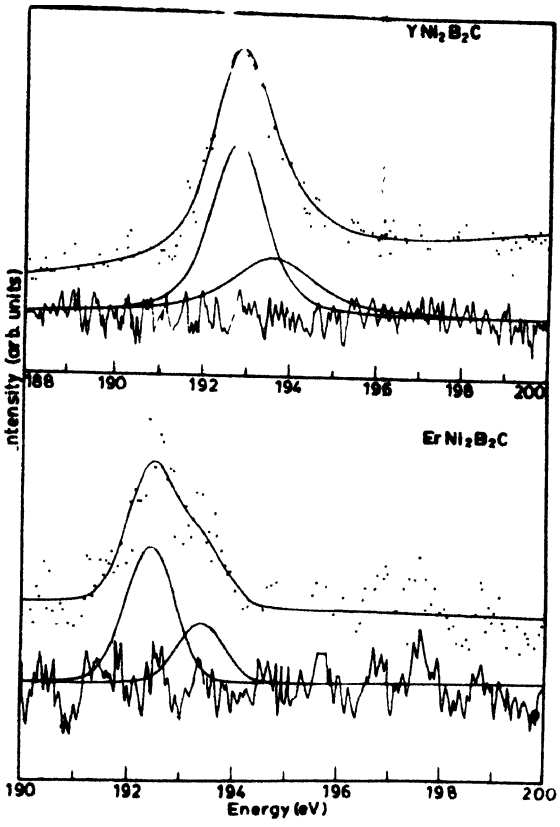

Figure 1. XPS spectra of B 1*s* for YNi_2B_2C and $ErNi_2B_2C$.

level is 187.3 eV. The observed energy of B 1*s* core level appears to also lie close to B 1*s* core level binding energy in B_2O_3 which is ~192–193 eV. Hence, we can infer that this peak may also have contribution from the boron bonded strongly to the surface oxygen. The observed increase in binding energy or strengthening of bonds of boron is apparent from the chemistry of boron. Because of incomplete octet, repulsions between non-bonding electrons may be somewhat less than normal, permitting closer approach of bonded atoms. This may also be due to B–O bonds, which have high bond energies because of large electronegativity differences.

Ni 2p core level :

The background subtracted spectra for YNi_2B_2C show that the Ni 2*p* core level binding energy for Ni $2p_{3/2}$ peak occurs at 852.9 eV and for Ni $2p_{1/2}$ at 870.35 eV. We have then deconvoluted the spectrum by creating a window from 848 to 860 eV to hold Ni $2p_{3/2}$ peak with its associated satellite structure (at 855.96 eV). After deconvolution, the Ni $2p_{3/2}$

peak is found to be at 852.89 eV with its satellite peak at 855.96 eV. When the *d*-orbitals are involved in the bond the XPS spectrum shows a structured satellite having binding

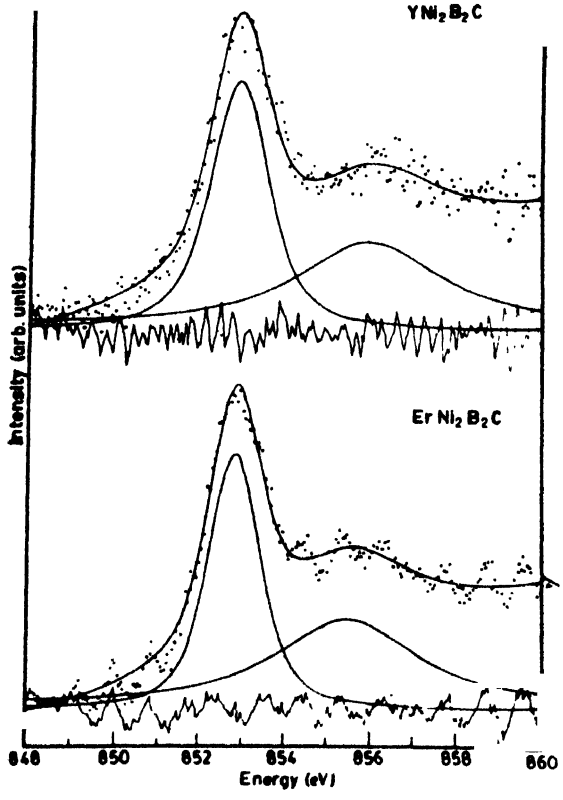

Figure 2. XPS spectra of Ni $2p$ (Ni $2p_{3/2}$ with its satellite structure) for YNi_2B_2C and $ErNi_2B_2C$.

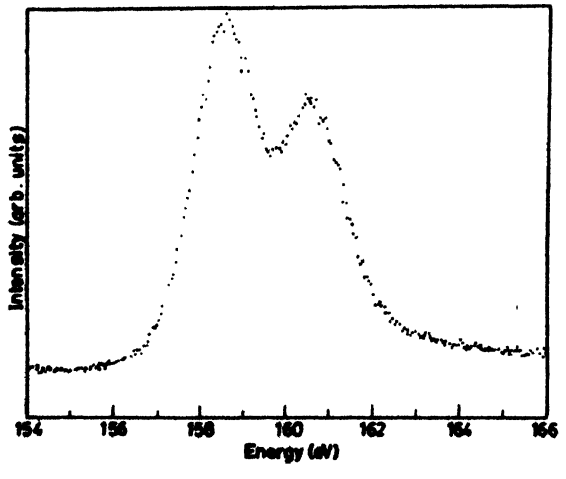

Figure 3. XPS spectra of Y $3d$ for YNi_2B_2C (raw data).

energy higher than the main line [10]. Band structure calculations on $LuNi_2B_2C$ by Pickett *et al* [2] and on YNi_2B_2C by Lee *et al* [4] also suggest strong hybridization between Ni 3*d* and B 2*p* orbital, giving a strong indication of its three dimensional character, strongly suggesting Ni to be in metallic state. Also, the distance between Ni–Ni atoms is 2.49 Å close to that of *fcc* Ni metal (2.50 Å) [4] suggesting that Ni is divalent in YNi_2B_2C.

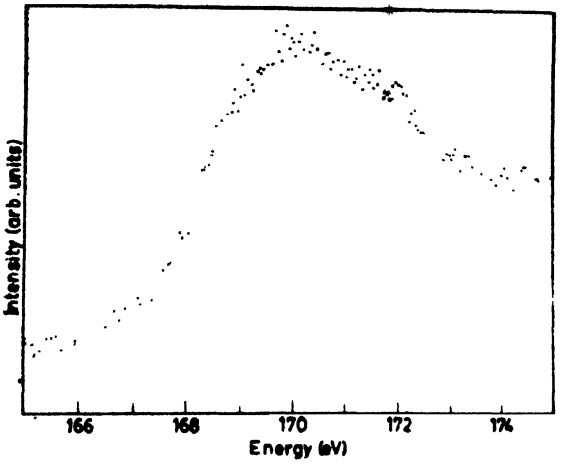

Figure 4. XPS spectra of Er 4*d* for $ErNi_2B_2C$ (raw data).

Similarly, for $ErNi_2B_2C$, Ni $2p_{3/2}$ peak occurs at 852.8 eV and Ni $2p_{1/2}$ occurs at 870.2 eV and after deconvolution, the Ni $2p_{3/2}$ peak is found to be at 852.8 eV with its satellite peak at 855.5 eV. The binding energy clearly corresponds to that of Ni^{2+} oxidation state. This again shows that Ni exists in its metallic state only and hence is divalent and does not show any sign of mixed valency.

Y 3d and Er 4d core levels :

The binding energy of Y $3d_{5/2}$ peak occurs at 158.6 eV which matches well with the binding energy of Y $3d_{5/2}$ in Y_2O_3 indicating that the valence of Y is 3+. This is in agreement with the work published by Gupta [11]. According to him, all the rare earth ions exist in trivalent state except Ce in these systems.

Figure 4 shows the binding energy peak of the XPS spectra of Er 4*d*. The value of Er $4d_{5/2}$ level is 169.4 eV and agrees well with the binding energy of Er $4d_{5/2}$ level for elemental Er. This indicates that Er exists in 2+ state or nearly 2+ state which is not in agreement with Gupta [11].

However, in both the compounds measurement of Y L_{III} and Er L_{III} edge XANES spectra is likely to be more conclusive on the question of valence state of Y and Er.

The core level binding energies have been studied for the quarternary borocarbide samples $ErNi_2B_2C$ and confirms Y and Er to be in a valence state of 3+ and 2+ respectively. The Ni spectra show that Ni stays in 2+ state in both the samples. We can

understand the electronic structure of quarternary borocarbides in detail by studying the valence of other rare earths in such systems.

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